SCIENCE AND TECHNOLOGY FOR ENERGY AND NATIONAL SECURITY

CRF NEWS

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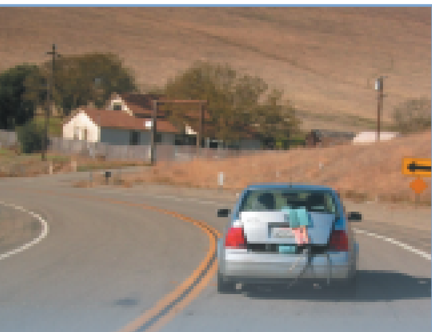

Particulate Emissions Measured On Board a Diesel Passenger Vehicle

Ability to Measure "Real-World" Emissions is Key to Validating Federal Vehicle Compliance Procedures

A CRF-led team of researchers has demonstrated the ability to measure "real-world" particulate emissions from a vehicle under actual driving conditions. While on-board measurements of gaseous emissions are routine, time-resolved particulate measurements have been far more elusive, yet are essential for validating federal emissions guidelines for vehicle compliance.

Pete Witze of the CRF Engine Combustion Department recently collaborated with Artium Technologies, Chevron Oronite, and the National Research Council (NRC) Canada to demonstrate the feasibility of obtaining on-board measurements of particulate emissions using laser-induced incandescence (LII) (see Figure 1). Artium's commercially-available LII instrument and ancillary equipment were placed in the trunk and on one side of the rear seat of a 2002 Volkswagen Jetta with automatic transmission and a turbocharged direct-injection (TDI) diesel engine.

(Continued on page 2)

CRF News At 25

Newsletter Celebrates 25 Years of Bringing Research News to the Combustion Community

With this issue of CRF News, we commemorate the 25th anniversary of the newsletter and recognize the upcoming anniversary of the Combustion Research Facility itself in 2005. CRF News was launched prior to completion of the CRF, which opened to visitors in November 1980. This editorial by Dan Hartley, the CRF's first director and a key player in its establishment, marks the first of a series of articles we will publish this year and throughout 2005, looking back at the CRF's history and accomplishments. When he retired in 2000, Hartley was Vice President for Laboratory Development. Look for other guest editorials in future issues as we celebrate this important milestone.

— Bill McLean, Director

Thirty years ago, the Combustion Research Facility was little more than an idea. It was an idea borne out of the energy crisis of the early 1970s, a shift in national research priorities toward energy research, and the development of several tools for use in the nation's nuclear weapons program with potential applications in studying the complexities of combustion.

As a researcher and supervisor at Sandia's Livermore facility back then, I was developing laser-based diagnostics to study the constituents of mixing gases as part of our weapons work. We recognized that this also might be a useful tool in analyzing combustion processes inside engines, and thought there was a chance we could establish a research institution at Sandia that would not only advance the science of combustion, but could do so in a lasting and respected way. Taz Bramlett, Bob Setchell, and I put together a formal proposal that started the ball rolling, and the leadership of Tom Cook and Arlyn Blackwell of Sandia, and Jim Kane, Karl Bastress, and Dominic Monetta of DOE's predecessor agency, the Energy Research and Development Administration, helped us advance the idea toward the concept of a national user facility.

If you ask me the point that gave us the unbreakable momentum, I would have to say it was our decision to host a concept review in the late 1970s (at the Hyatt Regency in San Francisco) where we invited university, industry, and government leaders in the field to help us design the facility and to set its desired culture. We also wanted to establish a dialogue and trust between us and the combustion community, which in some cases was somewhat wary and anxious about what we were doing and afraid that we might absorb government research dollars at its expense. At the time, we made a commitment to increasing visibility and support for combustion research, under the premise that a rising tide would lift all boats. And that indeed happened.

Sandia retiree Dan Hartley was the first director of the CRF.

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Emissions

(Continued from page 1)

An on-board diagnostics (OBD) scan tool interface was used to access the vehicle and engine speeds for recording while the vehicle was driven on a test route in the Livermore Valley. These measurements were then time-matched with the LII measurements to obtain a synchronized data set correlating time-resolved particulate emissions with vehicle operating conditions that included city driving, freeway driving with entrance-acceleration and hill ascent, and coasting descent on a rural road.

The most interesting result was obtained during the coasting descent from the Altamont Pass, as shown in Figure 2. Although the vehicle speed and engine rpm are reasonably steady for the period from 470 to 600 seconds, the particulate emissions suggest that fuel injection cycled on and off intermittently. The researchers suspect that, in the desired operating mode, fueling would be turned off for the entire descent, but perhaps the need to keep the vehicle's oxidation catalyst warm requires intermittent fueling. The average particulate emissions measured by LII during this period were 8.4 ppb, as compared to 10–11 ppb during steady-state idle. This suggests that the engine control module has been programmed to minimize fuel consumption during a descent while maintaining idle-like particulate emission levels and an active catalyst.

The ability to measure on-road particulate tailpipe emissions is of growing environmental interest because of the desire to validate current U.S. Environmental Protection Agency (EPA) vehicle certification procedures. These procedures, which have been the industry standard for more than 30 years, measure emissions using a chassis dynamometer and specify engine loads and speeds to be applied during testing. Because such tests do not replicate variables encountered under actual driving conditions (e.g., grade changes, weather, etc.), the automotive industry expects dynamometer emissions testing to be supplemented with on-road measurements in the future.

In general, innovative new methods are needed to evaluate the effects of mobile source emissions—both from off- and on-road sources—on air quality, especially as the EPA and state agencies, such as the California Air Resources Board (CARB), update their mobile source emission models.

Figure 1. The research team with the Volkswagen Jetta test vehicle. From left: Will Bachalo and Greg Payne (Artium), Greg Smallwood (NRC), Pete Witze (CRF), Gary Hubbard (consultant), Brian Graskow (Chevron), and Mike Fidrich (Artium).

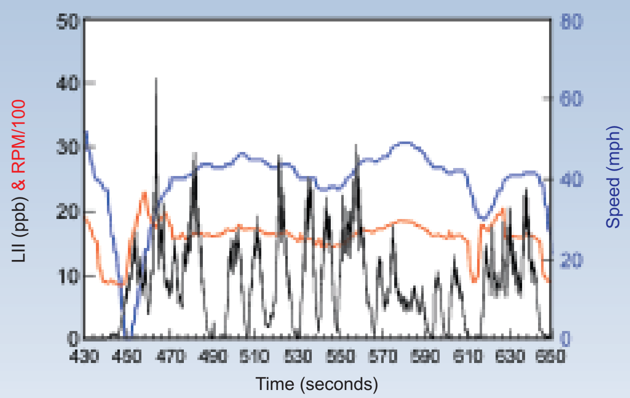

Figure 2. LII and engine and vehicle speed measurements for the coasting descent

25 Years

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Combustion Research Facility NEWS

CRF NEWS LAUNCHED--

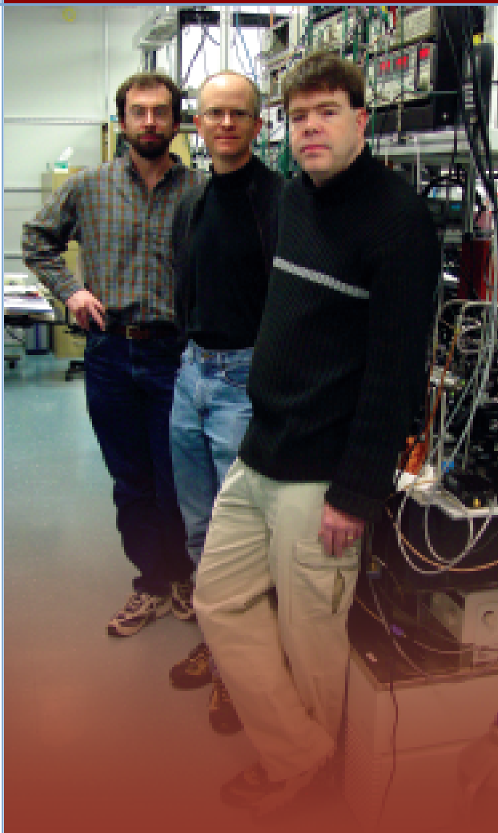
DOE REVIEWS SANDIA COMBUSTION RESEARCH

CONSTRUCTION UNDER WAY ON CRF

CRF News debuted in 1979 to keep the combustion community informed and involved with the CRF.

In March 1979, we launched the *Combustion Research Facility News*, a bimonthly newsletter designed "to keep the combustion research community abreast of the facility construction, research plans and progress, and visitor opportunities," as I wrote in the inaugural issue. At the time, construction of the CRF was underway, and an advisory board, composed of representatives from industry and universities, had been appointed. In November 1980, the staff moved into their offices, and the first users were welcomed to the facility.

In looking back, there may have been some visionary decisions made by a lot of people, but that only got it started. The real praise goes to all of the researchers, then and now, who have continued to pursue the highest quality work, in partnership with others, and with commitment to peer publication and participation. The CRF News keeps that message alive and well.



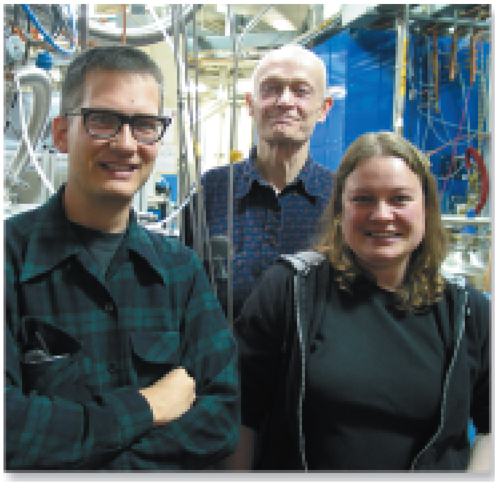
Joakim Bood (right), a postdoctoral research associate in the Combustion Chemistry Department since 2001, has taken an academic appointment in the Department of Combustion Physics at the Lund Institute of Technology, in Lund, Sweden. While at Sandia, Joakim worked with Andy McIlroy (center) and David Osborn (left), developing an ultrasensitive absorption spectrometer that combines cavity enhancement with frequency modulation spectroscopy. This technique holds promise for sensitive detection in chemical kinetics and low-pressure flame experiments.

Advisory Board Conducts Annual Review

The CRF Advisory Board conducted their annual review of CRF programs Nov. 6–7, 2003. CRF managers and technical staff provided the board with a broad overview of CRF research along with several more detailed research highlights.

Appearing in the photo above, left to right, are Bob Carling, CRF deputy director; board member Chris Sloane, director, FreedomCAR and Advanced Technology Strategy, General Motors Research & Development; Jay Keller, manager, Hydrogen and Combustion Technologies; Ed Law, Department of Mechanical and Aerospace Engineering, Princeton University, and president of the Combustion Institute; Greg McRae, Chemical Engineering Department, Massachusetts Institute of Technology; Sarah Allendorf, manager, Combustion Chemistry; Bob Gallagher, recently retired CRF manager; Ron Hanson, Department of Mechanical Engineering, Stanford University; Bill McLean, CRF director; Andy McIlroy, manager, Reacting Flow Research; Dennis Siebers, manager, Engine Combustion; Wen Hsu, manager, Remote Sensing and Energetic Materials. Board member John Stringer of EPRI was unable to attend.

Board members Ron Hanson, Chris Sloane, Ed Law, and Greg McRae visit the lab of CRF scientist Dahv Kliner.



Tina Kasper, a graduate student with Katharina Kohse-Höinghaus at the University of Bielefeld (Germany), has just completed a six-month visit during which she collaborated with Sandians Craig Taatjes (left) and Andrew McIlroy (not shown) on studies of fundamental flame chemistry. During her visit, she analyzed rich, low-pressure flames of ethanol and propanol. Part of her work involved using synchrotron photoionization molecular beam mass spectrometry in a low-pressure flame apparatus operating at the Advanced Light Source at Lawrence Berkeley National Laboratory (LBNL), where this photo was taken. The LBNL work is part of a collaboration with Cornell University professor Terrill Cool (center) and Prof. Phillip Westmoreland of the University of Massachusetts.

From left to right: John Daily (University of Colorado at Boulder), Volker Sick (University of Michigan), Helmut Kronemayer, and Christof Schulz (both of the University of Heidelberg) worked with Tom Settersten at the CRF in December as part of an ongoing collaboration that began in September 2002. The group is using picosecond pump-probe experiments to study population cycling in laser-induced fluorescence (LIF) detection of nitric oxide. Results of these experiments will guide their treatment of electronic quenching in a comprehensive computer model they are developing for NO LIF.

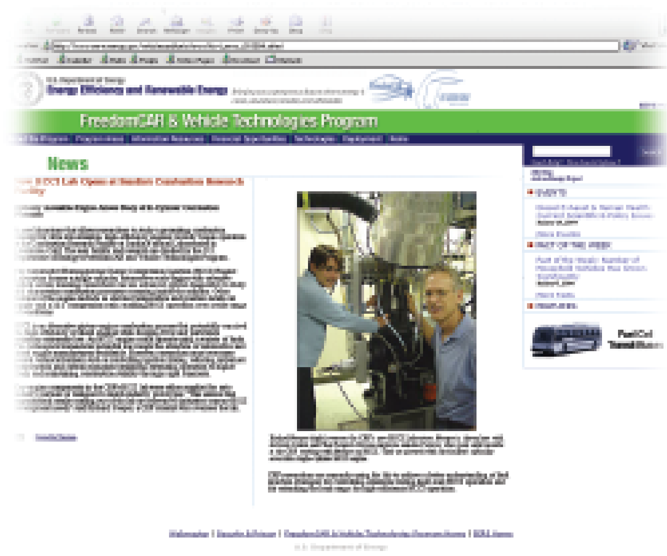
The following article also appeared on the Department of Energy FreedomCAR and Vehicle Technologies Program Web site ***(www.eere.energy.gov/vehiclesandfuels)*** *in January.*

New Homogeneous Charge Compression Ignition Lab Opens

Optically Accessible Engine Allows Study of In-Cylinder Combustion Processes

A new laboratory that allows researchers to study a promising combustion concept for ultra low-emission, high-efficiency engines recently began operation at the CRF. The new facility and research are funded by the U.S. Department of Energy's FreedomCAR and Vehicle Technologies Program.

The Automotive Homogeneous Charge Compression Ignition (HCCI) Engine Laboratory houses a single-cylinder, automotive-scale engine with extensive optical access, meaning researchers can use advanced optical diagnostics to study and characterize combustion processes occurring inside the cylinder. Other features of the engine include an elevated temperature and pressure intake air supply and a 12:1 compression ratio, enabling HCCI operation over a wide range of conditions.



HCCI is an alternative piston-engine combustion process that potentially can rival the high efficiency of diesel engines while keeping NOx and particulate emissions extremely low. An HCCI engine could operate using a variety of fuels. The technique's tremendous potential has caught the attention of automotive and diesel engine manufacturers worldwide. However, researchers must overcome several technical barriers, such as controlling ignition timing, reducing unburned hydrocarbon and carbon monoxide emissions, extending operation to higher loads, and maintaining combustion stability through rapid transients.

Key engine components in the CRF's HCCI lab were either supplied by auto industry partners or designed to match industry prototypes. "This assures that experimental results coming out of the lab are relevant to industry's current HCCI development needs," said Richard Steeper, a CRF scientist who oversees the lab.

CRF researchers are currently using the lab to achieve a better understanding of fuel injection strategies for controlling emissions during light-load HCCI operation and for extending the load range for high-efficiency HCCI operation.

Sandia and PPG Industries Focus on Chemistry of Tin Oxide Glass Coating to Improve Process Efficiency

The deposition of tin oxide coatings during float glass manufacturing is a complex process that enables the production of low-emissivity windows, solar cells, and flat-panel displays. However, the high speed of flat-glass production lines makes the coating process difficult to optimize and control. Researchers at the CRF and PPG Industries are working to improve process efficiencies by developing a better understanding of the chemistry of this oxidation process as well as computational models that can predict coating defects.

The Sandia team, consisting of Yong Kee Chae, Bill Houf, and Tony McDaniel, and led by Mark Allendorf, recently completed an extensive set of experiments, providing the most comprehensive set of growth-rate data available for SnO_2 deposition from the commonly used precursor monobutyltintrichloride ($C_4H_9SnCl_3$; MBTC). Lack of well-characterized experimental data was a major stumbling block at the outset of the program, which began two and half years ago with funding from DOE's Office of Industrial Technologies.

Such data are critical to the development of models. High float-glass line speeds require fast coating growth rates (1–3 s) and high volumetric gas flows to achieve uniform coating over large substrate areas (up to 4 m wide). These conditions lead to low reactant conversion efficiencies (as low as 10%).

While deposition temperature and reactant concentration have significant effects on growth rate, other requirements, such as the need to minimize haze and to control coating color, hinder the manipulation of these variables to enhance coating efficiency. In addition, the difficulty and cost involved in making changes to a full-scale manufacturing line underscores the need for models that predict the effects of process variables on deposition rate and reactant utilization.

The growth-rate data using MBTC were obtained using a new stagnation-flow reactor (SFR) that provides exceptional control over deposition parameters (substrate temperatures vary by less than ± 7 K across most of the substrate). In addition, the SFR design is advantageous for chemical vapor deposition because it can be modeled using one-dimensional codes such as CHEMKIN/SPIN, and the uniform fluxes across the substrate provide a wide area of uniform deposition rates. Such reactors are now widely used in the microelectronics industry for these reasons.

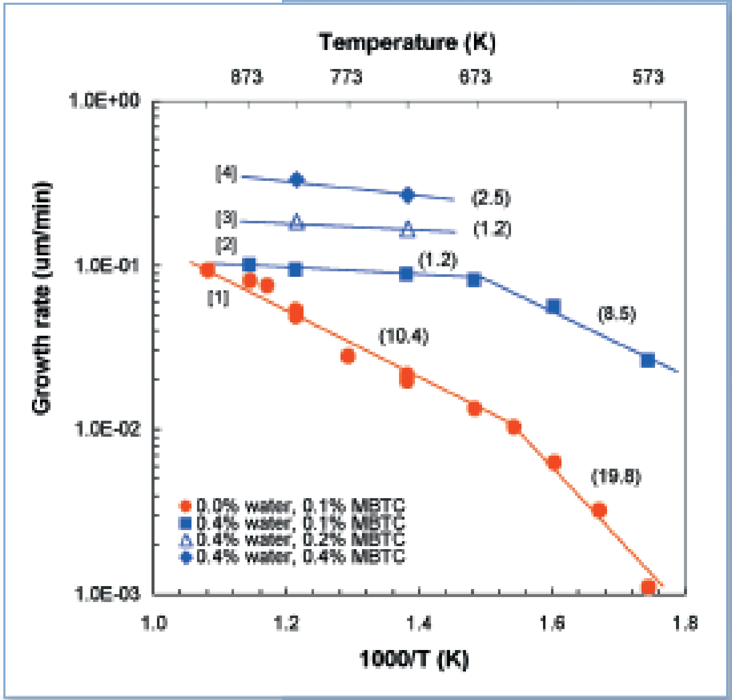


Figure 1. Comparison of growth rates obtained from MBTC + O_2 and MBTC + O_2 + H_2O mixtures at a total pressure of 25.0 Torr, total flowrate of 5.0 std l/min, and 20.0 mol% O_2. The number in parentheses represents the activation energy in kcal mol^{-1}.

Key results of the experiments are data demonstrating the accelerating effect of water on the SnO_2 growth rate. As seen in Figure 1, growth rates increase markedly when H_2O is mixed with MBTC and oxygen. At the lowest deposition temperature used (573 K), the deposition rate increases by a factor of 20 when H_20 is added, with smaller increases seen as the temperature increases. By 673 K, growth enters a mass transport-limited regime. Although this effect has been observed previously, these experiments provide the first insight into the nature of the chemistry leading to tin oxide deposition.

At all but the highest temperatures used, previous ab initio modeling of the tin chemistry (see *CRF News*, May/June 2002) indicates that MBTC does not thermally decompose. Thus, the increase in growth rates with H_20 addition is caused either by an exceptionally fast gas-phase reaction between MBTC and H_2O, leading to a highly surface-reactive precursor, or by activation of the growth surface through adsorption of H_2O. Quantum-chemistry calculations using the Bond Additivity Correction (BAC-MP4) method for tin compounds devel-

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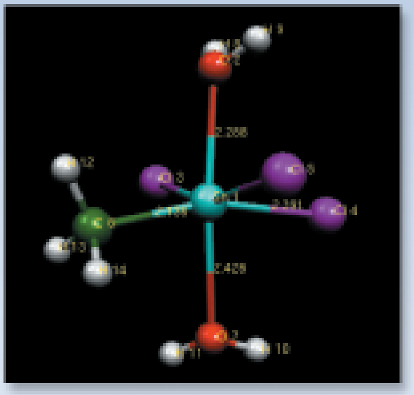

Figure 2. Geometry of a gas-phase complex between an analog of the tin oxide precursor MBTC and two H_2O molecules, as predicted by the BAC-MP4 ab inito quantum chemistry method.

Partnership to Pursue Research for Next-Generation Engines

Advanced engine combustion and emissions research leading to the next generation of efficient, clean engines is the focus of a new partnership involving Sandia, four other national laboratories, and 10 automotive and heavy-duty diesel engine manufacturers.

The memorandum of understanding (MOU) is designed to bring several research efforts under one umbrella to more effectively pursue a common goal of improved engine efficiency while maintaining compliance with relevant emission regulations.

Participants in the research effort include Caterpillar Corporation, Cummins Corporation, DaimlerChrysler Corporation, Detroit Diesel Corporation, Ford Motor Company, General Electric Global Research Center, General Motors Corporation, International Truck, John Deere, Mack Trucks Inc., Argonne National Laboratory, Lawrence Livermore National Laboratory, Los Alamos National Laboratory, Oak Ridge National Laboratory and Sandia.

Research will target low-temperature, clean combustion strategies, such as homogeneous charge compression ignition and various forms of stratified charge compression ignition combustion, and advanced diesel combustion strategies, such as multiple injections and high exhaust gas recirculation rates. The program will also focus on combustion and emissions research in support of the development of high-efficiency, low-emission hydrogen-fueled engines.

Researchers hope to develop a knowledge base of in-cylinder mixing, combustion, and emission processes relevant to advanced engine combustion and fuel injection strategies. They also hope to develop models for predicting these processes. Both are necessary for developing the next generation of efficient, clean engines.

Fuels to be considered in the program will include conventional fuels, non-petroleum based fuels and hydrogen.

For more information, contact Dennis Siebers, manager, Engine Combustion Department, (925) 294-2078, siebers@sandia.gov.

Tin Oxide

(Continued from page 5)

oped by Carl Melius and Allendorf suggest that exothermic complex formation can occur when H_2O interacts with an organometallic tin compound. An example of this is shown in Figure 2. In this case, formation of $CH_3SnCl_3(H_2O)_2$ is exothermic by 16 kcal mol^{-1}. Experiments and modeling are now underway to determine whether this pathway or a completely heterogeneous process is the more likely mechanism.

TNF7 Workshop To Be Held in Chicago

The Seventh International Workshop on Measurement and Computation of Turbulent Nonpremixed Flames (TNF7) will be held July 22–24 in Chicago. Information is available at **www.ca.sandia.gov/TNF**

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